Kinetic Mechanism for Pyrolysis of Acetylene Near 1000K

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INTRODUCTION

Recently a mechanism for acetylene pyrolysis was proposed to describe experimental data obtained from a single-pulse shock tube (1) over the temperature range of 1100 to 2000K. The kinetic mechanism is similar to those proposed previously (2,3) and includes mechanisms to describe formation of vinylacetylene, benzene, and phenylacetylene. Subsequently, a subset of this mechanism was modified and used (4) to match decay profiles of acetylene as well as product formation for pyrolysis data obtained in a flow reactor (5) at temperatures of 873 to 1173K.

It is the objective of this study: (a) to extend the mechanism (4) to include formation of higher molecular weight species, with a detailed discussion of growth from one to two rings; (b) to discuss the possible role of the 'odd' radical, i-C_4H_3; (c) to discuss some uncertainties with modeling PAH formation.

Description of Model

The kinetic model used in this study is listed in Table I and contains 89 reactions and 43 species. CHEMKIN and LSODE were used for integration of the rate equations. For modeling of the flow reactor data, constant temperature and pressure conditions were imposed whereas, for the shock tube data, a shock tube code modified (1) to simulate quenching in a single-pulse shock tube was utilized.

Thermodynamic parameters (except for those of vinyl radicals) are the same as those used and reported previously (1) for the lower molecular weight species. Parameters for species with molecular weights above 100 AMU were obtained from Stein (6) and are believed to be identical to those used in Frenklach, et. al. (3) Reference data for vinyl radicals and heavier species are reported in Table II. Stein's thermodynamic data for vinyl radicals were adopted since his heat of formation (68.4 kcal/mole) is higher than that used by Colket (1) (65.7 kcal/mole) and is closer to some recent determinations. In addition, Stein's reference value for entropy is higher (by 2 eu) than that used by Colket. Fortunately, the differences in values are nearly offset when determining equilibrium constants ($\ln K_{eq} = -(\Delta H - T\Delta S)/RT$) and changes in chemical kinetic modeling results are minimal.

The chemical kinetic model differs from that used previously (4) in that C_2H, C_4H_2, C_4H, i-C_4H_3, C_6H_2 and C_6H and associated reactions were included. In addition, species and reactions related to formation of polycyclic aromatics were also added. Of particular note is a modification in the dominant bimolecular initiation step. Previously the reaction

$$C_2H_2 + C_2H_2 \rightleftarrows n\text{-}C_4H_3 + H$$

was used with a rate constant of log (k/sec^{-1}) = 14.54 - 68000/4.58T. In the present study the reaction

$$C_2H_2 + C_2H_2 \rightleftarrows i\text{-}C_4H_3 + H$$

which has a lower endothermicity was employed with a rate of log (k/sec^{-1}) = 14.54-60500/4.58T. This larger rate constant for initiation is required to counterbalance termination steps omitted previously.

Formation of Fused Rings

This work was guided substantially by the significant contributions of Bittner, Howard, and Palmer (7) and of Frenklach, et. al (3). An important conclusion of the former work is that ring growth is dominated by addition of aryl radicals to triple bonds, followed by addition of acetylene to the resultant vinyllic (aromatic) radical, cyclization, and loss of an H-atom.

i.e.,

$$\dot{\phi} + C_4H_2 \rightleftarrows \phi CH\dot{C}CH$$

$$\phi CH\dot{C}CH + C_2H_2 \rightleftarrows \phi CHC(CCH)CH\dot{C}H$$

$$\phi CHC(CCH)CH\dot{C}H \rightleftarrows$$  $$\rightleftarrows H +$$ 

Other than reverse processes, the main competitive process which can inhibit ring growth is the thermal decomposition of the vinyllic adducts (i.e., loss of H-atoms). Bittner, et. al, reached specific conclusions regarding the importance of the thermal decomposition of the vinyllic adduct relative to its addition to acetylene. However, these conclusions may have to be re-examined, since calculations were based on low pressure flame conditions rather than those of a high pressure combustor.

Frenklach, et. al, included at least six separate reaction sequences for growth from a single to a fused ring. One reaction sequence, however, was found to dominate although a second played a minor, but contributing role. The second (minor) reaction sequence is comparable to that proposed by Bittner, et. al (see above) although phenyl radicals add to acetylene, rather than diacetylene. The dominant reaction sequence was found to be initiated by H-atom abstraction from the ortho position on phenylacetylene, followed by acetylene addition and cyclization.

$$\dot{\phi}CCH + C_2H_2 \rightleftarrows \phi(CCH)CH\dot{C}H$$

$$\phi(CCH)CH\dot{C}H \rightleftarrows$$ 

The resultant aryl radical can subsequently add to triple bonds to continue growth to higher order polycyclic aromatics. Due to the lack of experimental

rate data for reactions involving abstraction, addition, cyclization, or ring fracturing of polycyclic aromatics, Frenklach, et. al, selected generic rate constants for classes of reaction.

Rate constants for reactions involving aromatic species as listed in Table I were selected using the same technique of Frenklach, et. al, i.e., rate constants for a class of reactions are equated. Previously (3), values for several of these classes were assigned since experimental data was sparse. In this study, we have where possible updated the reaction rate data to be consistent with recently available determinations.

Predictions from the model (at 973K, 20% acetylene, and one atmosphere) are compared to the data from Munson and Anderson (5) in Fig. 1 for acetylene decay and production of benzene. In Fig. 2, predictions of production of styrene, naphthalene, and phenanthrene are shown. Although there is no experimental data from Munson and Anderson for these species, the final concentration of naphthalene is similar to other results (8) near 1000-1100K. The predicted value for styrene is about a factor of ten high.

Initially, only the dominant and minor mechanism (as identified by Frenklach, et. al) were included in the reaction sequence, specifically Mechanisms I and II:

I $\quad \phi C_2H + R \rightleftharpoons \dot{\phi}C_2H + RH \qquad (A)$

$\dot{\phi}C_2H + C_2H_2 \rightleftharpoons \phi(C_2H)CH\dot{C}H$

$\phi(C_2H)CH\dot{C}H \rightleftharpoons A2$

and

II $\quad \phi C_2H + H \rightleftharpoons \phi CH\dot{C}H \qquad (B)$

$\dot{\phi} + C_2H_2 \rightleftharpoons \phi CH\dot{C}H \qquad (C)$

$\phi CH\dot{C}H + C_2H_2 \rightleftharpoons \phi CHCH\dot{C}H$

$\phi CHCH\dot{C}H \rightleftharpoons A2H + H$

where A2 represents the 1-naphthyl radical and A2H, naphthalene.

The net contribution of the second sequence to the formation of A2H (or A2) dominates over that of the first by several orders of magnitude. For the specific conditions considered in this study, this fact can be easily explained.

At the low temperature (≈1000K) and the high initial concentrations of acetylene, forward reaction rates can be shown to dominate. Ignoring the contribution of Reaction C and taking the radical, R, in Reaction A to be an H-atom, then the relative rate is simply the rate of H-atom abstraction from the ring by H-atoms relative to the rate of H-atom addition to the acetylenic group in phenylacetylene. The value (9) of k ($C_6H_6 + H \rightarrow C_6H_5 + H_2$)

at 1000K is about 10^{10} cc/mole-sec. The rate constant for H-atom addition to acetylene, according to Ellul, et. al (10), extrapolates to 2 x 10^{12} cc/mole-sec at 1000K. Using these rate constants as estimates for k_A and k_B, respectively, Mechanism II is approximately 200 times faster than the first. The dominance of the Mechanism II becomes more apparent when the contribution of Reaction C is considered, since Reaction C is two to three orders of magnitude faster than Reaction B. Consequently, the second sequence is more than four orders of magnitude faster than the first. This is opposite to the trend observed by Frenklach, et. al. This strong discrepancy can be explained by a combination of (a) the higher temperatures of their study which enhance thermal decomposition of the radical adducts; (b) the lower partial pressures of acetylene in their study (40 torr vs. 150 torr in this study) which reduce the rate of radical addition to acetylene; and (c) the use by Frenklach of a high, temperature independent rate constant for Reaction A (with R as H-atom). Their rate constant was selected to be 10^{14} cc/mole-sec whereas, Kiefer, et. al's expression (9) gives 1.6 x 10^{12} cc/mole-sec at 1600 K.

Consequently, a reanalysis of dominant reactions occurring in a practical device should be performed for the specific ambient conditions. A preliminary analysis of the kinetic model indicates that the Mechanism II will dominate at temperatures of 1500-1700K for high pressure combustors, in which local acetylene concentrations may be at least an order of magnitude larger than considered in this and and previous studies.

Also found to contribute a minor but significant role at 973K are the overall reactions

$$\dot{\phi} + C_4H_4 \rightarrow A2H + H$$

and

$$\phi C_2H + i\text{-}C_4H_3 \rightarrow A2C_2H + H$$

both of which require H-atom shifts prior to cyclization. The second of these could be part of a very attractive sequence (as shown in Fig. 4) depending on the concentration of $i\text{-}C_4H_3$ radicals.

Role of $i\text{-}C_4H_3$

It is recognized that thermochemistry plays a significant role in the ability to model the above processes. Frenklach, et al. (11) have demonstrated quantitatively that uncertainties in thermochemistry drastically affect computed results. An interesting and possibly important thermochemical aspect of acetylene pyrolysis is due to the rather large difference between the heats of formation of the two isomers of C_4H_3, i.e., HCCCHĊH and HCCĊCH$_2$. The separation in this work was taken to be 10 kcal/mole, although Stein (6) and Bittner (12) give 8 and 15 kcal/mole, respectively. Due to its relative stability, the isomer with the unpaired electron on the secondary carbon atom ($i\text{-}C_4H_3$) becomes a dominant radical in the acetylene system. The situation is exacerbated if an isomerization step ($i\text{-}C_4H_3 \rightleftarrows n\text{-}C_4H_3$) is not included. Depending on temperature, the

concentration of i-C_4H_3 is two to three orders of magnitude higher than that of its isomer and an order higher than that of the vinyl radical. Consequently, it is logical that i-C_4H_3 plays a significant role in termination, and quite possibly in ring formation and growth.

The importance of this radical to chain termination or to ring formation and growth is dependent critically on (a) the thermodynamics of the C_4H_3 isomers; (b) the isomeration rate (equated in this work to a rate suggested (13) for the i-propyl⇄n-propyl isomeration); and (c) rate constants for reactions forming and destroying i-C_4H_3. Reactions which dominate formation of i-C_4H_3 include H-atom abstraction from vinylacetylene by phenyl, vinyl and H-atoms. The principal destruction mechanism in the present study is the isomerization to n-C_4H_3.

Uncertainties

Significant uncertainties in both rate constants and mechanisms still exist. The initiation step in acetylene pyrolysis has been a matter of unresolved dscussion for nearly thirty years. There is perhaps just as much uncertainty in the termination step(s). In this work, recombination of C_2H_3 + C_2H_3, H + C_2H_3, i-C_4H_3 + i-C_4H_3, and H + i-C_4H_3 all contributed to termination, yet there is essentially no data available on the absolute value of their rate constants (although some information on reverse reactions is available). The addition of H-atoms to acetylene is critically important to this mechanism, yet there is no data on this reaction near or above 1000K. Rate constants for reactions of similar types have been equated in this work; however, changes in rate constants depending on molecular size may be quite significant. Molecular and ionic processes have been ignored in the present study; however, there is as yet no proof against their occurrence. It is believed, however, that due to the reasonable agreement between the present model and experiments, contributions due to such reactions are perhaps small.

Conclusions

A chemical kinetic model, revised to include growth of aromatic rings predicts profiles of acetylene decay and formation of benzene, vinylacetylene, ethane, and hydrogen which are in agreement with experimental flow reactor results near 1000K. In addition the model predicts the formation of styrene, phenylacetylene, naphthalene and other fused rings. An analysis of the detailed model indicates that the dominant route for growth from a single to a fused ring is due to addition of phenyl radicals to two acetylenes. Addition of phenyl to vinylacetylene was proposed and may play a significant role depending on pressure and relative concentrations. Uncertainties associated with the role of the i-C_4H_3 radical were discussed and a mechanism involving sequential addition of i-C_4H_3 to phenylacetylene and the resultant products was proposed as a conceptually attractive mechanism for ring growth. Uncertainties related to the heat of formation and rate of isomerization to n-C_4H_3 prevent quantitative predictions as to the importance of such a mechanism.

Acknowledgements

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TABLE I
REACTIONS FOR ACETYLENE PYROLYSIS NEAR 1000K
logk = logA + nlogT - E/R/T/2.303 *

	Reactions	Forward Rate Constant			Reverse Rate Constant		
		logA	n	E	logA	n	E
1	2C2H2=i-C4H3+H	14.54	0.0	60.5	13.49	0.0	0.2
2	H+C2H2=C2H3	12.92	0.0	2.7	12.96	0.0	41.6
3	C2H3+C2H2=n-C4H5	12.88	0.0	8.0	14.86	0.0	44.1
4	n-C4H5=C4H4+H	13.00	0.0	33.0	12.39	0.0	-5.4
5	n-C4H5+C2H2=ℓ-C6H7	12.18	0.0	5.0	14.25	0.0	41.0
6	c-C6H7=ℓ-C6H7	14.48	0.0	50.0	11.36	0.0	0.4
7	C6H6+H=c-C6H7	13.60	0.0	4.3	13.12	0.0	24.6
8	C2H3+C4H4-C6H6+H	11.60	0.0	0.0	0.00	0.0	0.0
9	C4H4+n-C4H5-A1C2H3+H	13.50	0.0	5.0	0.00	0.0	0.0
10	A1C2H3+H=A1C2H2S+H2	14.00	0.0	14.5	13.09	0.0	19.7
11	C2H4+C6H5=A1C2H3+H	11.57	0.0	2.1	12.92	0.0	1.4
12	C6H6+H=C6H5+H2	14.40	0.0	16.0	12.39	0.0	9.5
13	C2H2+C6H5=A1C2H2	12.00	0.0	4.0	13.72	0.0	42.2
14	C2H3+C4H4=C2H4+n-C4H3	13.00	0.0	10.0	13.09	0.0	9.5
15	C4H4+C6H5=C6H6+n-C4H3	12.48	0.0	0.0	13.04	0.0	3.1
16	ℓ-C6H5=n-C4H3+C2H2	13.40	0.0	36.1	11.11	0.0	0.0
17	C6H5=ℓ-C6H5	13.54	0.0	65.0	10.25	0.0	1.7
18	C2H3+C6H6=C2H4+C6H5	13.48	0.0	13.0	13.00	0.0	9.3
19	2C2H3=C4H6	13.40	0.0	0.0	17.15	0.0	104.9
20	C4H4=n-C4H3+H	15.00	0.0	100.0	12.91	0.0	-7.9
21	C6H6=C6H5+H	15.70	0.0	107.9	13.05	0.0	-3.2
22	n-C4H5+H=C4H4+H2	13.00	0.0	0.0	12.99	0.0	66.0
23	n-C4H5+H=C4H6	13.00	0.0	0.0	14.84	0.0	107.9
24	n-C4H5+n-C4H3=2C4H4	12.70	0.0	0.0	14.18	0.0	69.5
25	n-C4H5+C2H3=C4H4+C2H4	12.00	0.0	0.0	13.57	0.0	69.0
26	C2H3+H=C2H4	12.85	0.0	0.0	15.00	0.0	107.2
27	C6H5+C2H3=A1C2H3	12.60	0.0	0.0	16.11	0.0	106.5
28	C2H3+H=H2+C2H2	13.00	0.0	0.0	13.57	0.0	65.5
29	C2H4+H=C2H3+H2	14.84	0.0	14.5	13.30	0.0	11.7
30	C4H4+H=n-C4H3+H2	13.90	0.0	14.5	12.42	0.0	11.0
31	C4H6+H=n-C4H5+H2	14.00	0.0	14.5	12.76	0.0	10.9
32	C4H6+C2H3=n-C4H5+C2H4	13.18	0.0	10.0	13.52	0.0	9.5
33	C6H5+C6H6=C12H10+H	11.80	0.0	11.0	13.38	0.0	9.2
34	C2H4+M=C2H3+H+M	16.16	0.0	81.8	14.01	0.0	-25.4
35	2i-C4H3=C4H4+C4H2	11.00	0.0	0.0	14.35	0.0	47.8
36	i-C4H3+H2=C2H2+C2H3	10.70	0.0	20.0	11.18	0.0	14.8
37	C4H4=i-C4H3+H	15.20	0.0	95.0	12.72	0.0	-2.1
38	C2H+C4H4=C2H2+i-C4H3	13.60	0.0	0.0	12.48	0.0	27.9
39	n-C4H3=C2H2+C2H	14.30	0.0	57.0	13.56	0.0	3.0
40	i-C4H3=C4H2+H	12.00	0.0	49.0	12.86	0.0	-0.2
41	n-C4H3=C4H2+H	12.60	0.0	40.0	13.04	0.0	1.4
42	n-C4H3=i-C4H3	13.00	0.0	35.0	12.58	0.0	45.7
43	i-C4H3+H=C4H2+H2	13.00	0.0	0.0	14.47	0.0	55.2
44	n-C4H3+H=C4H2+H2	12.48	0.0	0.0	13.53	0.0	65.9

* NOTES: Units for A: cc,moles,sec., Units for E: kcal/mole.
= represents forward and reverse directions included in model.
- represents forward direction only included in model.

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TABLE I (continued)
REACTIONS FOR ACETYLENE PYROLYSIS NEAR 1000K
logk = logA + nlogT - E/R/T/2.303 *

	Reactions	Forward Rate Constant			Reverse Rate Constant		
		logA	n	E	logA	n	E
45	C4H4+H=i-C4H3+H2	14.49	0.0	14.5	12.62	0.0	21.9
46	C6H5+C4H4=C6H6+i-C4H3	12.18	0.0	0.0	12.31	0.0	13.8
47	C2H3+C4H4=C2H4+i-C4H3	12.70	0.0	10.0	12.36	0.0	20.2
48	C4H4=C2H+C2H3	15.70	0.0	115.0	12.93	0.0	-7.8
49	H2+M=2H+M	12.35	-.5	92.5	11.74	-.5	-11.9
50	C2H2+M=C2H+H+M	16.62	0.0	107.0	15.25	0.0	-17.9
51	C2H+H2=H+C2H2	12.85	0.0	0.0	13.60	0.0	20.5
52	C2H+C2H2=C4H2+H	13.60	0.0	0.0	14.78	0.0	15.4
53	C2H+C4H2=C6H2+H	13.60	0.0	0.0	14.97	0.0	15.1
54	C4H+C2H2=C6H2+H	13.30	0.0	0.0	14.91	0.0	8.1
55	C4H+H2=H+C4H2	13.30	0.0	0.0	14.30	0.0	13.5
56	C6H+H2=H+C6H2	13.30	0.0	0.0	14.53	0.0	10.3
57	C2H+C6H6=C6H5+C2H2	13.30	0.0	0.0	12.05	0.0	14.1
58	C4H+C6H6=C6H5+C4H2	13.30	0.0	0.0	12.29	0.0	7.0
59	C2H3+C4H2=C4H4+C2H	13.48	0.0	23.0	13.70	0.0	5.4
60	2C6H5=C12H10	12.48	0.0	0.0	16.57	0.0	108.3
61	C2H+C4H4=C2H2+n-C4H3	13.60	0.0	0.0	12.91	0.0	17.2
62	A1C2H3+H=A1C2H2+H2	14.50	0.0	14.5	13.29	0.0	11.7
63	A1C2H2S=A1C2H+H	13.00	0.0	45.0	13.11	0.0	0.8
64	A1C2H2=A1C2H+H	12.30	0.0	37.0	12.71	0.0	0.8
65	A1C2H2+C2H2=A1C4H4	12.88	0.0	8.0	14.81	0.0	44.5
66	A1C4H4=A2H+H	10.00	0.0	0.0	13.32	0.0	18.5
67	C6H5+C4H4=A2H+H	11.60	0.0	0.0	17.14	0.0	56.4
68	A1C2H+C2H3=A1C2HP+C2H4	13.70	0.0	13.0	14.02	0.0	10.5
69	A1C2H+H=A1C2HP+H2	14.40	0.0	16.0	13.18	0.0	10.7
70	A1C2H+C2H=A1C2HP+C2H2	13.30	0.0	0.0	12.85	0.0	15.2
71	A1C2H+i-C4H3-A2C2H+H	11.60	0.0	0.0	0.00	0.0	0.0
72	A1C2H+C2H3-A2H+H	11.60	0.0	0.0	0.00	0.0	0.0
73	A1C2HP+C4H4=A1C2H+i-C4H3	12.18	0.0	0.0	11.51	0.0	12.6
74	A1C2HP+C2H2=A1C2HV	12.30	0.0	4.0	13.70	0.0	41.8
75	A1C2HV=A2	11.00	0.0	0.0	14.14	0.0	53.4
76	A2C2H2=A2C2H+H	12.30	0.0	37.0	12.71	0.0	0.8
77	A2+C2H2-A2R5+H	12.30	0.0	4.0	0.00	0.0	0.0
78	A2C2H2+C2H2=A2C4H4	12.88	0.0	8.0	14.81	0.0	44.5
79	A2C4H4=A3H+H	10.00	0.0	0.0	13.32	0.0	20.7
80	A2H+H=A2+H2	14.40	0.0	16.0	12.88	0.0	10.7
81	A2H+H=A2P+H2	14.40	0.0	16.0	12.88	0.0	10.7
82	C2H3+A2H=C2H4+A2	13.70	0.0	13.0	13.72	0.0	10.5
83	C2H3+A2H=C2H4+A2P	13.70	0.0	13.0	13.72	0.0	10.5
84	A2P+C2H2=A2C2H2	12.30	0.0	4.0	13.70	0.0	41.8
85	A2C2H+H=A2C2HX+H2	14.40	0.0	16.0	13.49	0.0	10.7
86	A2C2H+C2H3=A2C2HX+C2H4	13.70	0.0	13.0	14.33	0.0	10.5
87	A2C2HX+C2H2-A3	12.30	0.0	4.0	0.00	0.0	0.0
88	A3+C2H2-A4H+H	12.30	0.0	4.0	0.00	0.0	0.0
89	A3H+H=A3+H2	14.40	0.0	16.0	13.18	0.0	10.7

* NOTES: Units for A: cc,moles,sec., Units for E: kcal/mole.
= represents forward and reverse directions included in model.
- represents forward direction only included in model.

TABLE II
Selected Thermodynamics at 300K
(from Stein(6))

Species	Identification	Heat of Formation (kcal/mole)	Entropy (eu)
C2H3	vinyl	68.4	56.5
A1C2H3	styrene	35.3	82.6
A1C2H2	A1CHCH	91.2	85.2
A1C2H2S	A1CCH2	83.2	83.8
A1C2H	phenylacetylene	75.2	76.4
A1C2HP	A1C2H	133.6	79.0
A1C2HV	A1(C2H)CHCH	146.6	95.1
A1C4H4	A1CHCHCHCH	104.7	98.0
A2	1-naphthyl	94.4	83.6
A2P	2-naphthyl	94.4	83.6
A2H	naphthalene	36.1	79.7
A2C2H	2-naphthylacetylene	91.5	90.9
A2C2H2	A2CHCH	107.4	99.7
A2C2HX	A2C2H	149.9	92.1
A2C4H4	A2CHCHCHCH	121.0	112.5
A2R5	acenaphthylene	61.7	87.2
A3	phenanthrenyl	108.5	96.8
A3H	phenanthrene	50.1	94.2
A4H	pyrene	55.2	96.5

FIG. 1 MODEL PREDICTIONS vs. DATA OF REF. 5
C2H2 and C6H6 Concentrations at 973K

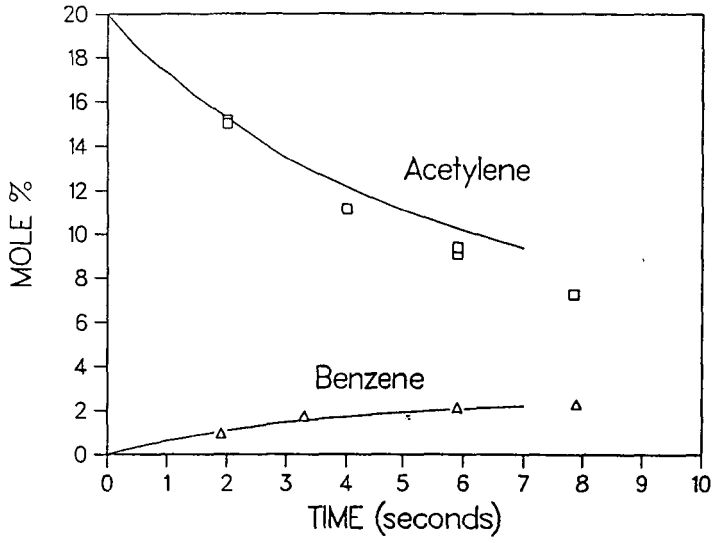
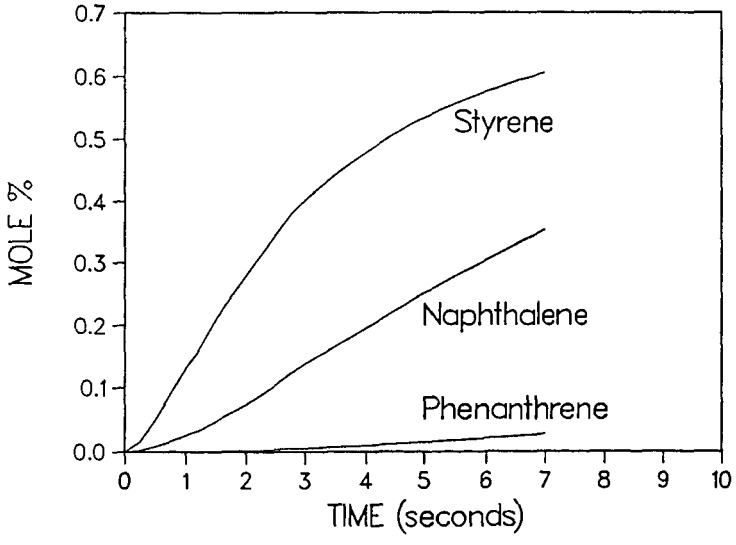


FIG. 2 PYROLYSIS OF 20% ACETYLENE AT 973K
Formation of Aromatic Products (predictions)



RING GROWTH BY SEQUENTIAL ADDITION OF i-C_4H_3

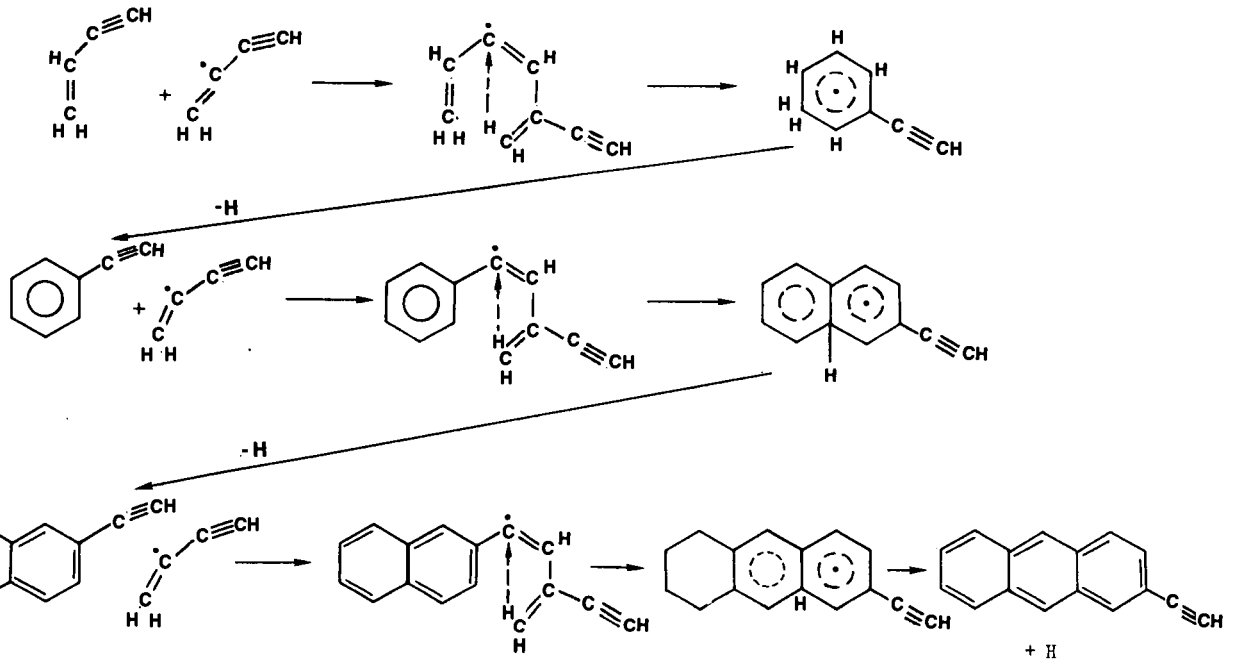


FIG. 3

87-4-89-1